

Effects of Alicyclic Ethylene Double Bond on the Optical Properties of Polyimide Films

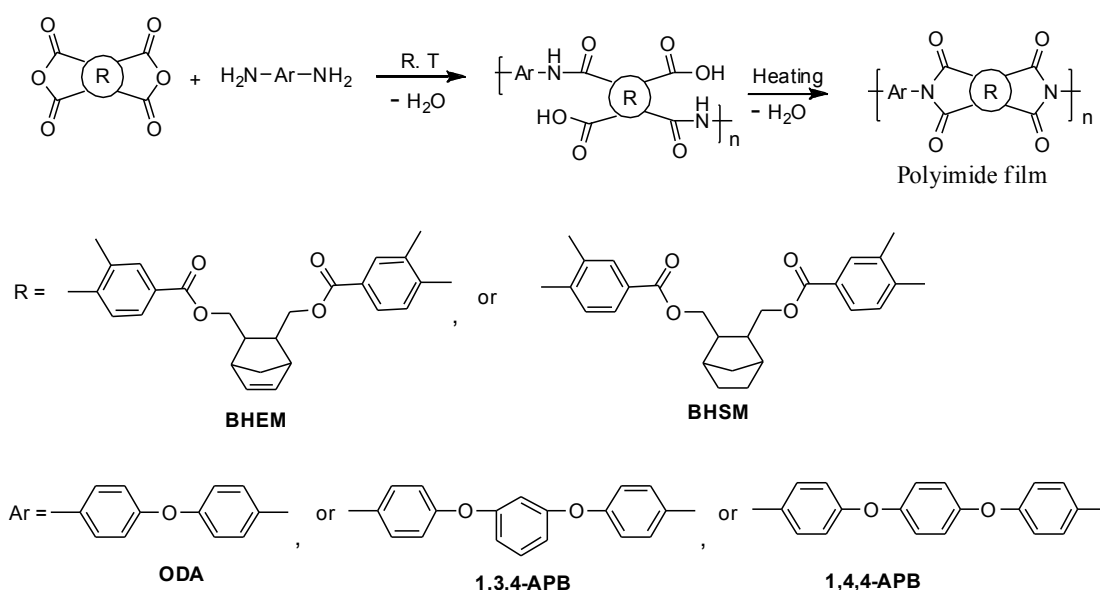
An-ran Zhang, Hai-xia Qi, Feng Liu *

Department of Chemistry, Nanchang University, 999 Xuefu Road, Honggutan New District, Nanchang, Jiangxi 330031, PR China

E-mail: liuf@ncu.edu.cn

Unlike the exhaustive research of unsaturated functional group in thermosetting polyimides, the application and effects of the unsaturated functional group in thermoplastic polyimides have rarely been studied. Meanwhile, considering the wide application of the alicyclic polyimides in microelectronics and optoelectronics, the significance of investigating the effect of the unsaturated alicyclic structure on the properties of the thermoplastic polyimide films becomes increasingly urgent.

In this work, six polyimide films were prepared by conventional two-step polycondensation of three commercial diamines, 4'-diaminodiphenyl ether (ODA), 1, 3-bis(4-aminophenoxy) benzene (1, 3, 4-APB) and 1, 4-bis(4-aminophenoxy) benzene (1, 4, 4-APB), with bicyclo[2.2.1]hept-5-ene-2, 3-diylobis(methylene)bis(1, 3-dioxo-1, 3-dihydroisobenzofuran-5-carboxylate) (BHEM) and bicyclo[2.2.1]heptane-2, 3-diylobis(methylene)bis(1, 3-dioxo-1, 3-dihydroisobenzofuran-5-carboxylate) (BHSM), respectively. For convenience, the polyimide films derived from BHEM with ODA, 1, 3, 4-APB and 1, 4, 4-APB are coded as PI-N1, PI-N2, and PI-N3, respectively, and the corresponding BHSM-derived polyimide films are coded as PI-S1, PI-S2 and PI-S3, respectively. The synthesis of the polyimides is shown in Scheme 1.



Scheme 1. The synthesis of the polyimide films (PI-Ns, PI-Ss)

When fully imidized after curing under 250 °C for 2 hours, the films of PI-Ns experience a more intense coloration than the films of PI-Ss. It infers that the oxidation of alicyclic ethylene double bond in BHEM has taken place during this process. The UV-Vis spectra of the fully imidized polyimide films are displayed in Fig. 1. It can be seen that PI-Ss have higher transmittance than PI-Ns. The influence of the diamines on the UV-vis transmittance of PI-Ns is remarkable. 1, 3, 4-APB endows the highest transparency, ODA follows, and 1, 4, 4-APB-derived polyimide films shows the poorest transparency. In comparison, the structure of the diamines shows less influence on the transparency of PI-Ss. Generally, these polyimide films show the cutoff wavelength ranging from 391-415 nm. The films PI-Ss have the transmittances at 500 nm in the range of 49% to 53%, whereas the films PI-Ns show the values of 19% to 36%.

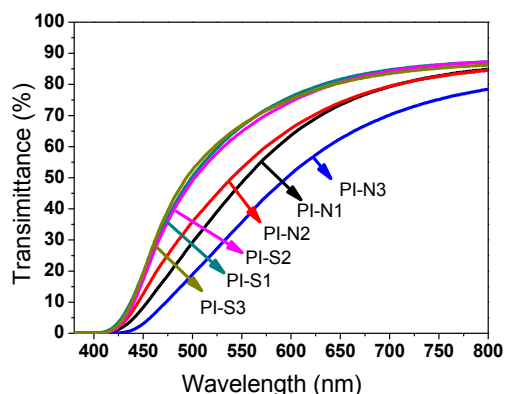


Fig. 1. The UV-Vis spectra of polyimide films

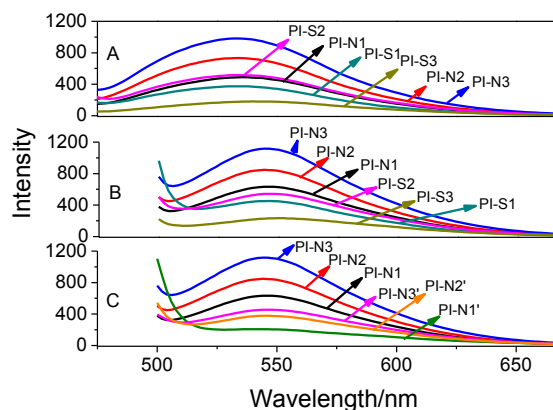


Fig. 2. The fluorescence emission spectra of PIs

As was clarified, the fluorescence of the fully aromatic polyimides originates from the strong charge transfer (CT) interactions, and their lowest excited states are attributable to CT (π - π^*) states, which emit weak fluorescence in longer wavelength than 450 nm. For the polyimides derived from aromatic dianhydrides having delocalized π conjugation and an alicyclic diamine, the lowest excited states are attributable to locally excited (LE) (π - π^*) states, which emit strong fluorescence in shorter wavelength than 400 nm. As is shown in Fig. 2, the fluorescence emissions of PI-Ns and PI-Ss were centered on the wavelength longer than 500 nm. Therefore, considering the backbone structures of the polyimide films and judging from the emission wavelength, the films of PI-Ns and PI-Ss emit CT fluorescence, and the Stokes shift is observed for 450 nm excitation (Fig. 2.A) and 490 nm excitation (Fig. 2.B), whose emission peaks were located around 535 nm and 545 nm, respectively.

The alicyclic ethylene double bond and the structure of the diamines basically show no influences on the CT fluorescence emission peak position, but show slight influences on the emission intensity. It was found that CT fluorescence intensity of the polyimide films has positive correlation with the degree of coplanarization of the polymer backbone. In comparison with the tetrahedral sp^3 configuration of alicyclic ethyl single bond in BHSM for PI-Ss, the sp^2 hybrid orbit of the alicyclic ethylene double bond in BHEM lead to increased coplanarization for the PI-Ns polymer backbone. Therefore, PI-Ns possess higher CT fluorescence emission intensity than PI-Ss for excitation both by 450 nm and by 490 nm. Likewise, the structure of symmetric diamine 1, 4, 4-APB has better coplanarization degree than its unsymmetric isomer 1, 3, 4-APB, which leads to a higher emission intensity of the PI-N3 than PI-N2. However, for PI-Ss series, 1, 4, 4-APB results in the lower CT fluorescence intensity of PI-S3 than 1, 3, 4-APB does for PI-S2. This may be associated with the poor film forming property of PI-S3, and that the fragile morphology of the film may decrease the intensity of CT fluorescence emission in a degree. Further thermal cure of PI-Ns at 300 °C (Fig. 2.C) decreases the CT emission intensity, indicating that some unfavorable thermal reaction for the CT fluorescence emission would have taken place during the thermal crosslinking of the alicyclic ethylene double bond leading to the reduced quantum yield.

In conclusion, the effects of alicyclic ethylene double bond in the main chain on the optical properties of the thermoplastic polyimide films were comparatively studied. We found that the planar sp^2 hybrid configuration of the alicyclic ethylene double bond impart the polymer chain with polarity and interchain CT interaction, which result in the increased coloration and emission intensity of CT fluorescence of the polyimide films.

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References

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